Evaluation of methane oxidation in a landfill cover material using a simple indicator approach

Jonathan A. Lafond and Suzanne E. Allaire*

Horticultural Research Centre,
Université Laval, 2480 Hochelaga,
Quebec, Qc G1V 0A6, Canada
Fax: (418) 656-7871
E-mail: jonathan.lafond.2@ulaval.ca
E-mail: suzanne.allaire@fsaa.ulaval.ca
*Corresponding author

Alexandre R. Cabral

Department of Civil Engineering,
Université de Sherbrooke,
2500 blvd de l'Université, Sherbrooke, Qc J1K 2R1, Canada
E-mail: alexandre.cabral@usherbrooke.ca

Abstract: Estimates of methane (CH_4) oxidation rates (R_g) in biocovers are crucial for development of abatement strategies. R_g values were estimated in a landfill biocover with a simple approach based on gas diffusion theory. R_g varied from 0 to 1.1×10^{-6} kg m^{-3} s^{-1}. Highest oxidation efficiencies reached 80–100% when soil water content < 40%, temperature > 20°C and O_2 concentration > 0.1 kg m^{-3}. R_g was correlated to oxidation efficiency measured by stable isotopes and surface emissions. The approach allows for affordable continuous monitoring of R_g, but only gives a rough estimate of CH_4 oxidation rate.

Keywords: gas diffusion; gas movement; oxygen; waste management; temporal variation; compost; landfill biocover; methanotrophic oxidation.

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Biographical notes: Jonathan A. Lafond is a PhD Student at the Département des sols et de génie agroalimentaire at Université Laval. He has been working on gas transport in soils, with special focus on multi-scale variability of gas diffusion. His interest includes different aspects of soil physics such as CT scanning, measuring methods and geostatistics with implications in several fields such as landfills and agriculture. He collaborates with several scientists in different research fields. His participation in the scientific community is ongoing with great interest in improving environmental health for present and future generations.

Suzanne E. Allaire is a Professor at the Département des sols et de génie agroalimentaire at Université Laval. She works on mass movement and preferential flow in porous media, with special focus on gas and contaminant

in soils. Her actual interest is multi-scale and multivariate spatio-temporal variability of soil physical properties and their impact on several environmental or engineering processes. She also develops preferential flow aspects of risk indicators of water contamination of a National Project (NAHARP). She has participated in various projects involving fluid flow in porous media. She teaches soil physics and hydrodynamics.

Alexandre R. Cabral is a Professor with the Civil Engineering Department, Université de Sherbrooke. He has more than 20 years of experience in landfill and mining research, with special focus on final cover design alternatives. He is also Project Manager for Groupe SM International, an engineering company from Quebec, which has offices in many countries. He has participated in various projects involving landfill final covers and mine reclamation projects. He teaches the following courses: Soil Mechanics, Sustainable Design and Environmental Management (Undergradutate) and Environmental Geotechnics (Graduate).

1 Introduction

Methane (CH_4) is an important Greenhouse Gas (GHG), with an effect 25 times higher than CO_2 in carbon equivalent over 100 years (IPCC, 2007a). Anthropogenic sources of CH_4 emissions are actually responsible for more than 60% of the total global budget, with landfills representing one of the largest contributors by nearly 23% in the USA (US Environmental Protection Agency, 2009) and 25% in Canada (Environment Canada, 2007). CH_4 constitutes from 50% to 60% of landfills biogases (Czepiel et al., 1996). Landfills are thus an important factor contributing for the drastic increase (almost triple) in atmospheric CH_4 concentration noted over the last 250 years.

Landfill biogases (mainly CO_2 and CH_4) can be intercepted by collection systems, which are far from being 100% efficient. In addition, gas collection systems are operated only for a relatively short period of time compared with the actual duration of biogas emissions (Humer and Lechner, 1999). They are turned off once they become uneconomical, which mean that subsequent CH_4 production constitutes fugitive emissions. Also, more than 75% of Canadian landfills are not equipped with a collection system and will not because they are either too old or too small. As a consequence, significant amounts of biogases escape as fugitive emissions during the lifetime of a landfill (e.g., Börjesson et al., 2007; Spokas et al., 2006).

Fugitive CH_4 emissions can be reduced by the action of methanotrophic bacteria, which are able to use molecular oxygen to oxidise CH_4 into CO_2 within the soil cover, also referred as biocover (Huber-Humer et al., 2008; Jugnia et al., 2008). Oxidation efficiencies can reach up to 90% of the CH_4 moving across the biocovers (Cabral et al., 2010; Gebert et al., 2003; Rannaud et al., 2009). Biocovers are viewed as an economically viable mean of reducing emissions in old and small landfills and as a complement to collecting systems. In fact, biocovers are cited in the IPCC Working Group III assessment report (IPCC, 2007b; Table SPM 3) as one of the key technologies for reducing fugitive landfill emissions.

However, much has to be learned about optimal conditions for methanotrophic oxidation. Besides the presence of CH_4, the presence of O_2 is a key parameter (Czepiel et al., 1996; Gebert et al., 2003). It has to diffuse from the surface into the substrate

to reach bacteria (Stępniewski and Zygmunt, 2000). This process is influenced by soil water content and bulk density because of their influence on air-filled porosity. CH_4 oxidation is also influenced by soil temperature, because of its impact on reaction rates and gas movement (Reay et al., 2001). Meteorological conditions such as air temperature, changes in barometric pressure and rainfall infiltration also influence CH_4 oxidation by affecting the movement of all gases. Nutrient availability is another factor for bacterial growth (Hilger and Humer, 2003). However, most of these parameters vary substantially with time, which renders estimates of variation in oxidation a rather difficult task; nonetheless, they are fundamental to improve GHG budget estimates and optimise gas management strategies.

Proper estimations of GHG emissions from landfills require an estimate of oxidation in the cover material. These estimations are usually performed using empirical models, some of which use a constant value for oxidation efficiency (the IPCC model). In addition, estimations vary substantially depending on the model used (Scharff and Jacobs, 2006). Briefly, they are not reliable. GHG budget estimated using empirical models may thus be greatly underestimated because of the large possible contribution of oxidation, irrespective of how widely it varies with time. On the other hand, continuous and reliable field estimation is complex and not easily available.

Several methods have been developed for estimating CH_4 oxidation. Some use isotope fractionation based on the increasing $^{13}C/^{12}C$ ratio related to the fact that bacteria oxidise ^{12}C-isotope preferentially to the ^{13}C-isotope (Mahieu et al., 2008). This approach is considered as the method of reference. However, its efficiency for estimating variations in oxidation is limited for several reasons, including the fact that it cannot be used in a continuous manner. Alternatively, one could estimate CH_4 oxidation by means of the evolution of the CH_4/CO_2 ratios along a gas profile. This ratio gives a rough idea of oxidation rates, but unknowns concerning the source of changes in CO_2 and O_2 (e.g., caused by soil respiration) render this approach rather imprecise. Another method that is under development and has recently been used to estimate the kinetics of CH_4 oxidation is the Gas Push-Pull Test (GPPT) (Gomez et al., 2009; Gonzalez-Gil et al., 2008; Urmann et al., 2005). A GPPT consists in the injection of a mixture containing CH_4 and O_2 and non-reactive tracer gases into the substrate, followed by extraction of the injected gases that mix with the air already in the substrate. Rate constants for CH_4 oxidation can be calculated by analysis of breakthrough curves of CH_4 and of an inert tracer gas (Urmann et al., 2005). Other approaches are based on gas movement for which many complex models have been developed (De Visscher and Van Cleemput, 2003; Metcalfe and Farquhar, 1987; Stein et al., 2001).

When advective fluxes can be considered negligible (Rannaud et al., 2009), a simple approach based on the diffusion theory can be used with *in situ* measurements of CH_4 concentrations, combined with easy-to-obtain parameters, such as water content and temperature. This type of approach is quite simple and inexpensive for routine measurements, as well as for the estimation of temporal variation in CH_4 oxidation rates. As a consequence, the development of a reliable simple method to estimate CH_4 oxidation rates within final covers constitutes an important contribution.

The goal of this study is to estimate CH_4 oxidation rates in an experimental biocover made of a sand–compost mixture using a simple approach based on gas diffusion and standard measurements such as soil water content, bulk density and gas concentrations. Relationships between calculated oxidation rates and some physical properties of this particular biocover are studied over two seasons (2006–2007). Results from a study

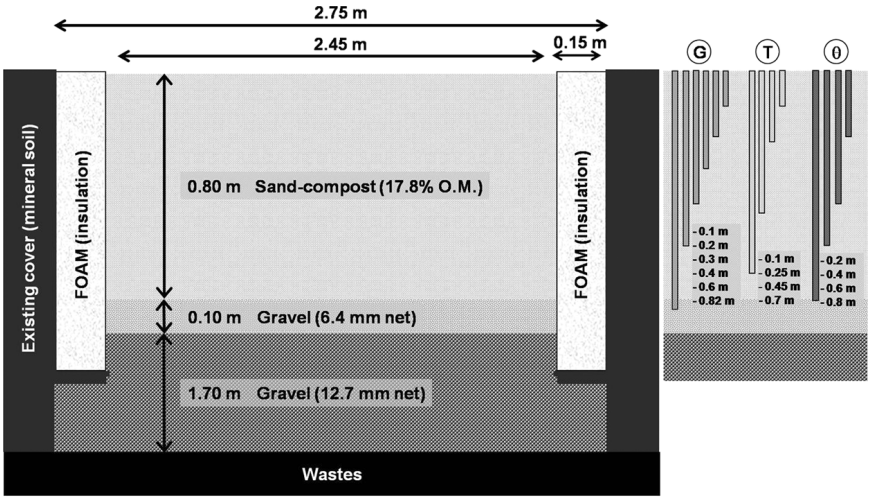
involving stable carbon isotopes (Cabral et al., 2010) and CH_4 surface emissions data for the same site are also used to validate the proposed approach.

2 Material and methods

2.1 Cell description

As part of an ongoing project aiming to study CH_4 oxidation in landfill covers, three experimental Passive Methane Oxidation Biocovers (PMOBs) were constructed and instrumented in June 2006 on a sanitary landfill near St-Nicéphore, Québec, Canada (45.814324 N, –72.376728 W). Monitoring data and results obtained from one of them (PMOB-1) are reported herein. PMOB-1's dimensions were 2.75-m wide × 9.75-m long. It was covered with a 0.80-m thick sand–compost mixture (Jugnia et al., 2008), herein referred to as substrate. The substrate was underlain by a 0.10-m thick transition layer consisting of 6.4-mm gravel. Below this layer, a thick Gas Distribution Layer (GDL), consisting of 12-mm gravel (Figure 1(A)), was constructed until the 3.5 years old waste mass was encountered. As a consequence, the PMOB-1 was fed in a passive manner with biogas coming directly from the waste mass. The GDL (Figure 1(A)) allows a good distribution of the incoming biogas. The walls around the PMOB were thermally shielded from the outside environment by 0.15-m thick polystyrene panels. The goal was to prevent lateral migration of moisture owing to thermal gradients, which could lead to preferential flow paths.

Figure 1 (A) Lateral cross-section of PMOB-1 and (B) schematic view in depth of the installed probes (*G*: gas probes; *T*: temperature sensors; *θ*: water content probes)



(A) (B)

The substrate material was composed of five volumes of compost (before sieving) and one volume of coarse sand (D_{10} = 0.07 mm; D_{85} = 0.8 mm; Cu = 4.3). The 2-year old compost consisted of a mixture of municipal sewage sludge, sludge from pulp of paper and agri-food industries (Jugnia et al., 2008). This composted material

was considered mature (Jugnia et al., 2008) according to Quebec standard (standard #0143-205-art 9.5, BNQ, 1997). The compost was sieved using an industrial mesh of 12 mm. The resulting organic matter content of the cover material was 17.8% ($g_{volatile\ matter}\ g^{-1}_{dry\ soil}$). The cover material was installed in four steps of 0.20-m thick layers successively compacted with a vibrating plate to an average bulk density of 839 kg m^{-3}.

Temperature sensors (TMC20-HD, from Onset), connected to a data acquisition system (HOBO U12, from Onset), volumetric water content sensors (EC-5, from Decagon), connected to another data acquisition system (EM-50, from Decagon) and gas probes (home-made aluminium tubes with an inner diameter of 10 mm that were capped at the top end with a septum), were permanently installed (Figure 1(B)) at four points along the slope gradient (separated by 1.8-m interval) and at four depths (six depths in the case of gas probes) in each profile. Meteorological data, including air temperature, precipitation, atmospheric pressure and wind speed, were continuously recorded by a weather station installed near the experimental cell. Temperatures were obtained in °C and then converted into °K to be used in the calculations presented herein. The average slope of the experimental PMOB was 3.5%.

Air-filled porosity (θ_a, $m^3\ m^{-3}$) and total porosity (Φ, $m^3\ m^{-3}$) of the substrate were calculated using the following equations (Jury and Horton, 2004):

$$\theta_a = \Phi - \theta_v \quad \Phi = 1 - \left(\frac{\rho_b}{\rho_s}\right) \tag{1}$$

where ρ_b is the bulk density (kg m^{-3}) and ρ_s is the empirical particle density for this material: 2290 kg m^{-3} (Blake and Hartge, 1986a). The degree of saturation in water at 0.2-m depth ($S_{w0.2}$) was calculated using the water content at saturation, i.e., 0.67 $m^3_{water}\ m^{-3}_{dry\ matter}$.

2.2 Monitoring periods

Temperature and water content values were collected every 30 min. Gas samples were taken from each probe at 1–3 weeks intervals, from July to October 2006 and from May to October 2007. Intensive sequences of gas measurement were performed from 5 to 6 September (24-hr sequence) and 12 to 14 September of 2007 (52-hr sequences), where samples were obtained from every probe at 1–4 hours intervals. Volumetric concentrations of CH_4, CO_2 and O_2 in the collected samples were obtained *in situ* using a portable landfill gas analyser (Portable Gas Meter, Columbus Instruments, OH) equipped with infrared sensors for CO_2 and CH_4 and with an electrochemical sensor for O_2. Meteorological data were recorded every 30 min by a weather station (Vantage Pro 2, Davis Instruments, CA, USA) installed on site near the experimental cell.

For this paper, only the data corresponding to 0.20-m depth were used for calculating CH_4 oxidation rates, because the oxidation front was situated most of the time between 0.10 and 0.30-m depths in this cell (Rannaud et al., 2009).

2.3 Relative gas diffusion coefficient (D_s/D_o)

The estimation of CH_4 oxidation rate in the biocover using Fick's law requires previous determination of the relative gas diffusion coefficient, D_s/D_o. To determine the latter, six intact cores were collected from the upper 0.20 m of the cell using PVC tubes of 0.10-m diameter × 0.076-m high (Blake and Hartge, 1986b). The cores were saturated with water and placed on tension tables to achieve desorption curve (Klute, 1986). The desorption curve was determined to measure the total porosity (Φ, $m^3\ m^{-3}$) and gas diffusion coefficient (D_s, $m^2\ s^{-1}$) at different water contents. The D_s in the cover material was measured for each step of the desorption curve using the unsteady state open chamber laboratory method (Allaire et al., 2008; Rolston, 1986) with argon as the tracer gas. Gas samples were withdrawn every 15 min for 3.5 h and analysed on a GC (Agilent Technologies, USA) equipped with a molsieve column and a TCD detector. Relative gas diffusion coefficient (D_s/D_o, unitless) was calculated with the coefficient of argon in air ($D_o = 2.0353 \times 10^{-5}\ m^2\ s^{-1}$) corrected for temperature (Roberts, 1972).

$$D_{T2,P2} = D_{T1,P1}\left(\frac{T_2}{T_1}\right)^{\alpha}\left(\frac{P_1}{P_2}\right). \tag{2}$$

Measured D_s/D_o were compared with 14 simple gas diffusion models (Table 1 in Allaire et al. (2008)). Root Mean Square Error (RMSE) and bias were calculated to respectively evaluate the average prediction uncertainty, and the intensity of over- or underestimation of D_s/D_o (Moldrup et al., 2005).

$$\mathrm{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N} d_i^2} \quad \mathrm{bias} = \frac{1}{N}\sum_{i=1}^{N} d_i \tag{3}$$

d_i is the difference between predicted and measured values of D_s/D_o at a given θ_a, and N is the number of measurements. Millington and Quirk (1961) best performed for this sand-compost material. D_s/D_o was then predicted for every θ_v measured in the biocover. A D_o value of $1.96 \times 10^{-5}\ m^2\ s^{-1}$ at 282 K (T_1) and at 1.013 bars (P_1) was used for estimating diffusion of CH_4 in air (Marrero and Mason, 1972; Roberts, 1972) and was corrected for soil temperature at 0.25 m (T_2) and barometric pressure (P_2) with an $\alpha = 1.76$ (Roberts, 1972; equation (2)).

2.4 CH_4 oxidation rate (R_g)

The following hypotheses were considered for the calculation of the CH_4 oxidation rate ($kg\ m^{-3}\ s^{-1}$):

- Fick's second law is applicable.
- Each individual measurement can be considered to have been taken under steady-state conditions.
- Advection is much lower than diffusion most of the time, such as found by Rannaud et al. (2009) for the same site. Whenever advection occurred, they showed that for low differential pressure such as 0.02 kPa, impact of flux variations on D_s was

estimated to be <20%. The substrate's gas permeability was also found to be low (in the vicinity of 10^{-13} m^2). All this combined to the fact that the gas collection system was fully functional in this capped area of the landfill support this hypothesis.

- O_2 is present at 0.2-m depth in sufficient concentrations for oxidation to occur.
- CH_4 abatement results only from microbial oxidation in the cover material.
- Counter-diffusion of oxygen downward does not affect CH_4 diffusion upward and vice versa.

CH_4 oxidation rates (R_g, kg m^{-3} s^{-1}) were estimated using the following analytical solution to Fick's second law, under steady-state condition:

$$R_g(z) = -\frac{2D_s(C_g(z) - C_o)}{(z^2 - z_L^2)} \tag{4}$$

where z is the depth (m), R_g is calculated at $z = -0.20$ m considering the reference point at the soil surface ($z = 0$), z_L is the lower limit of the profile ($z = -0.82$ m), $C_g(z)$ (kg m^{-3}) is CH_4 concentration at z corrected for temperature (equation (5)) and C_o (kg m^{-3}) is the initial CH_4 concentration at z_L, which is considered constant at 55% (m^{-3}_{CH4} m^{-3}_{air}) and also corrected for temperature as follows:

$$C_g(z) = C_{\%} \times \rho_{sg} \text{ where } \rho_{sg} = [(-0.0025 \times T_{soil}(K)) + 1.4066] \tag{5}$$

with the following boundary conditions.

$$\text{at } z = 0 \rightarrow \frac{\partial C_g}{\partial z} = 0 \quad \text{at } z_L = -0.82 \rightarrow C_o. \tag{6}$$

Despite the fact that CH_4 loading at the bottom of the PMOB fluctuates during the season, the CH_4 concentration measured in the raw biogas averages 55% and was quite constant. R_g was calculated for every gas sampling event of 2006 and 2007 and the uncertainty was considered at every step in the calculations.

2.5 Statistical analyses

The SAS-Stat software (version 9.1; SAS, 2002–2003) was used for statistical analyses. Variance homogeneity was tested using the UNIVARIATE procedure. Whenever not normally distributed, data show bimodal trends. The GLM procedure with repeated measures was used to estimate the effect of year, time and location in the cell. Regressions (PROC STEPWISE) were used to describe interactions between R_g and properties of the biocover. Since it is known that soil temperature is highly related to air temperature with certain attenuation and time lag (Jury and Horton, 2004), only the temperature at 0.25 m ($T_{0.25}$) was used in the regressions. Also, CH_4 concentration was not included in the regressions since it was directly used in the calculation of R_g.

3 Results and discussions

3.1 General trends

Seasons 2006 and 2007

The maximal calculated R_g values reached 1.1×10^{-6} kg m^{-3} s^{-1} and 2.3×10^{-7} kg m^{-3} s^{-1} while the minima were -6.2×10^{-8} kg m^{-3} s^{-1} and -9.6×10^{-9} kg m^{-3} s^{-1}, for 2007 and 2006, respectively. These minimal values are explained by a production of CH_4 instead of oxidation, which occurs under local anaerobic conditions that could be found during wet soil conditions. Maxima for 2007 were obtained from mid-July (DOY 196) to mid-August (DOY 220) (Figure 3). Other R_g peaks were found in mid-June (DOY 166), mid-May (DOY 140) and at the end of August (DOY 234). Maximal values of R_g appeared about 20 days later during the summer of 2006. They were much lower than maxima calculated for 2007. Oxidation tended to decrease to very low values from the end of August to the end of both fall seasons.

Considering the 0.80-m thick PMOB and the average air-filled porosity equal to 0.30 m^3_{air} m^{-3}_{soil} in 2007 and equal to 0.20 m^3_{air} m^{-3}_{soil} in 2006, the maximal R_g values were 22.8 g m^{-2} d^{-1} in 2007 and 3.2 g m^{-2} d^{-1} in 2006. These values correspond to those of Abichou et al. (2009) simulated from field data of a sandy soil (19.2 g m^{-2} d^{-1}) and a biocover made of compost (2.7 g m^{-2} d^{-1}) on a Florida landfill. As shown in Table 1, the average R_g for 2007 was 4.8×10^{-7} kg m^{-3} s^{-1} (or 9.95 g m^{-2} d^{-1} for a 0.80-m thick PMOB at an average air-filled porosity of 0.30 m^3_{air} m^{-3}_{soil}). R_g was expected to follow a sinusoidal function with time. Regression analyses indicate no sinusoidal relationship, but only a weak cubic function for 2006 ($r^2 = 0.76$*).

Several differences were observed between soil physical parameters of both seasons. The average $\theta_{v0.2}$ was almost 1.5 times higher in 2006 than in 2007 (Table 1). Gas concentrations (CH_4, CO_2 and O_2) were almost the same for both years, while temperatures were slightly higher in 2007 than in 2006 (Table 1). It is important to note that the duration of the sampling campaigns was not the same in each year: in 2006, it started in mid-July in 2006, whereas in 2007 sampling started in early May; this influences averages and tendencies, correlations and regressions between R_g and other parameters. As a consequence, the results of the two study periods were analysed separately.

R_g was almost 6 times higher in 2007 than in 2006 (Table 1, Figures 2 and 3). This can be partly explained by the fact that the experimental biocover was constructed in June 2006 and it took some time for full development and adjustment of the microbial population to its environment. Effectively, Jugnia et al. (2008) and Aït-Benichou et al. (2009) obtained an exponential evolution of the *pmo*A gene copy abundance from June to November 2006 in the same experimental cell indicating that the methanotrophs population was growing at 0.20-m depth during the entire season. Comparatively, methanotrophic bacteria populations were probably stabilised and fully functional for oxidation activity the following year. Thereafter, the discussion is mostly based on 2007 data.

Figure 2 CH_4 oxidation rates at 0.2-m depth in the biocover and related atmospheric and soil parameters for 2006 (error bars are incertitude associated to measurement precision)

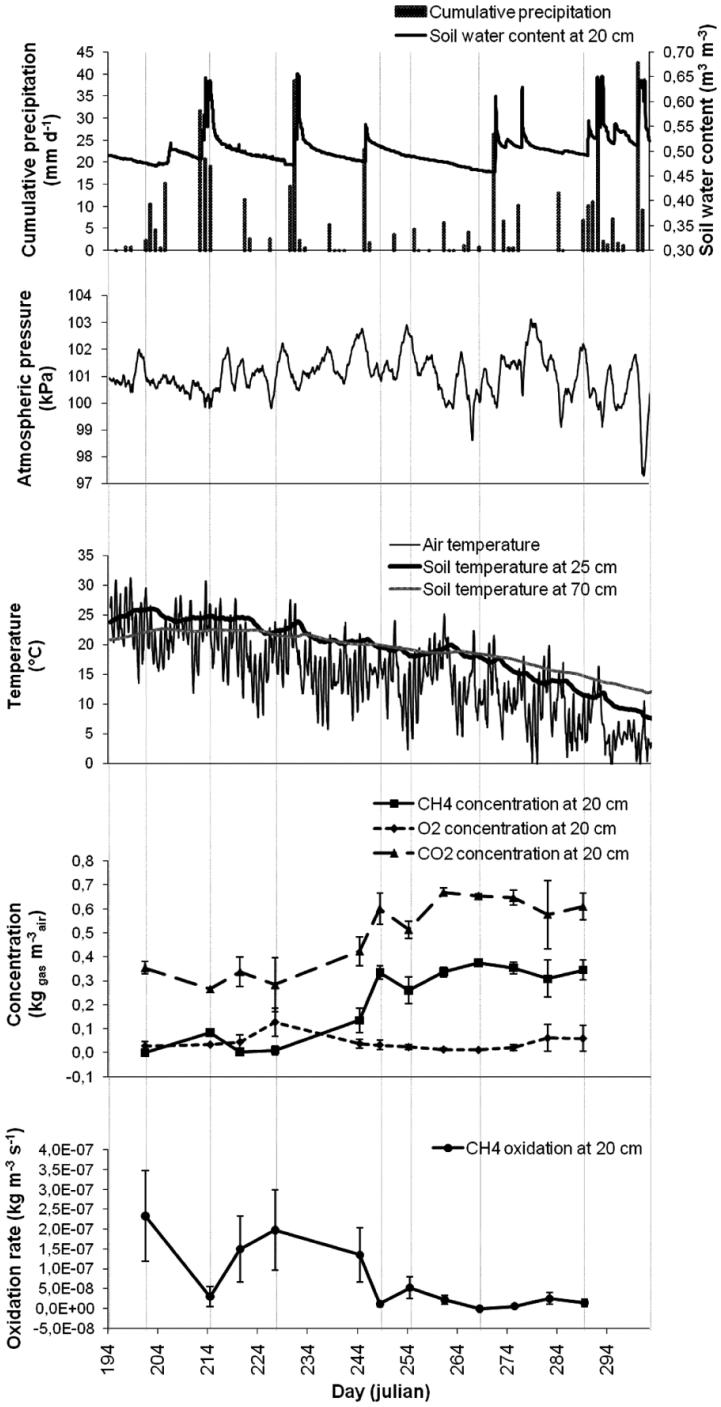
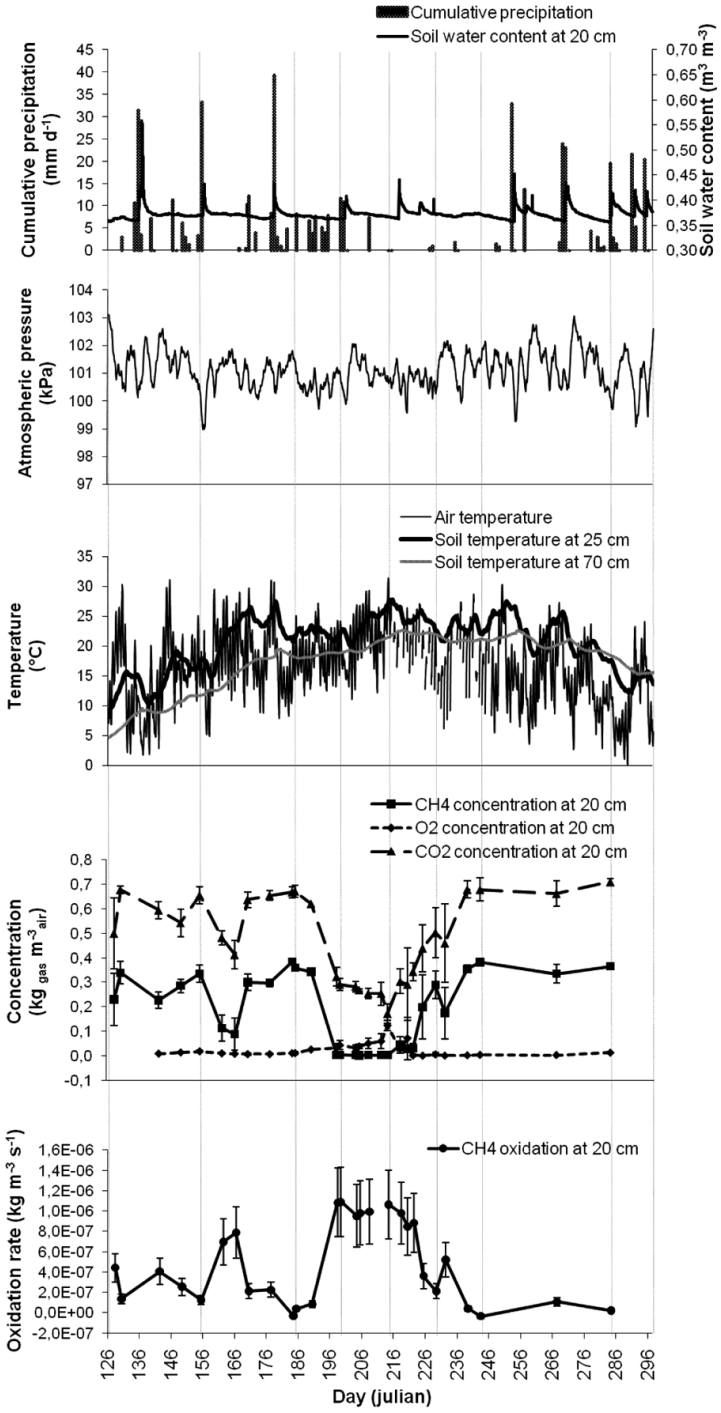


Figure 3 CH_4 oxidation rates at 0.2-m depth in the biocover and related atmospheric and soil parameters for 2007 (error bars are incertitude associated to measurement precision)



24-h and 52-h intensive sampling sequences

Higher oxidation rates were calculated during night-time of the 24-h sequence and during the afternoon of the 52-h sequence (Figures 4 and 5). R_g variations during this short time interval indicate that the time of the day during which gas samples are taken influences the estimated oxidation rate by almost 3-fold. Average R_g values (Table 1) of these sequences correspond to those found during the rest of 2007 (Figures 3–5). Oxidation rates were dependent on the sequence (24 or 52 h) ($F = 10.47$**). They were thereafter separately analysed. The general shape of the R_g functions was not sinusoidal in either sequence, but rather cubic ($r^2 = 0.37$**) during the 24-h sequence and no general trend could be found for the 52-h sequence (Figures 4 and 5).

Table 1 Descriptive statistics of oxidation rates (R_g) at 0.2-m depth and associated soil and atmospheric parameters for both years and sequences

	Statistical	R_g	CH_4	CO_2	O_2	T_{air}	$T_{0.25}$	T_{70}	$\theta_{v0.2}$ ($S_{w0.2}$)	*Prec.*	*P*
Time	*Parameters*	kg m^{-3} s^{-1}	kg m^{-3}	kg m^{-3}	kg m^{-3}	°C	°C	°C	m^3_{water} $m^{-3}_{dry\ m.}$	mm	kPa
Year											
2006	*N* (obs.)	45	45	44	45	48	48	48	29	48	48
	Min	–9.6E-09	0.5E-04	0.2	7.9E-03	9	11	14	0.41 (61%)	0	100.3
	Max	2.3E-07	0.4	0.7	1.7E-01	26	26	23	0.64 (95%)	0	102.9
	Mean	7.5E-08	0.2	0.5	3.9E-02	18	19	19	0.50 (75%)	0	101.3
	Std. dev.	8.3E-08	1.5E-01	1.5E-01	3.8E-02	6	4	2	0.07	0	0.8
	CV (%)	110	69	29	98	34	22	13	14	.	1
2007	*N* (obs.)	106	110	110	102	116	120	120	60	116	116
	Min	–6.2E-08	6.6E-04	0.1	0	12	9	5	0.33 (49%)	0	99.8
	Max	1.1E-06	0.4	0.7	1.8E-01	28	30	23	0.42 (63%)	0	102.5
	Mean	4.8E-07	0.2	0.5	2.1E-02	20	22	18	0.37 (55%)	0	101.2
	Std dev	4.1E-07	1.5E-01	1.8E-01	3.1E-02	4	4	5	0.03	0	0.6
	CV (%)	86	80	36	146	20	19	27	8	.	1
Sequence											
24-h	*N* (obs.)	38	38	38	38	40	40	40	20	40	40
	Min	4.4E-08	0.02	0.2	0	10	23	21	0.34 (51%)	0	101.6
	Max	1.0E-06	3.5E-01	0.7	4.1E-01	17	29	22	0.39 (58%)	0	101.8
	Mean	3.7E-07	0.2	0.6	2.5E-02	13	25	21	0.36 (54%)	0	101.8
	Std. dev.	2.9E-07	0.1	1.2E-01	6.7E-02	2	2	4E-01	0.03	0	0.1
	CV (%)	78	41	22	265	19	7	2	8	.	1E-01
52-h	*N* (obs.)	71	71	71	71	72	72	72	36	72	72
	Min	–4.0E-08	2.6E-03	0.2	1.3E-03	7	21	21	0.35 (52 %)	0	100.1
	Max	8.7E-07	0.4	0.7	9.6E-02	22	26	24	0.43 (64 %)	0	101.9
	Mean	2.1E-07	2.7E-01	0.6	1.9E-02	13	23	22	0.38 (57 %)	0	101.3
	Std. dev.	2.3E-07	0.1	1.1E-01	1.7E-02	4	1	1	0.03	0	0.5
	CV (%)	109	36	19	87	32	6	3	8	.	5E-01

Figure 4 CH_4 oxidation rates at 0.2-m depth in the biocover and related atmospheric and soil parameters during 24 h on 5–6 September 2007 (error bars are incertitude associated to measurement precision; precipitations = 0)

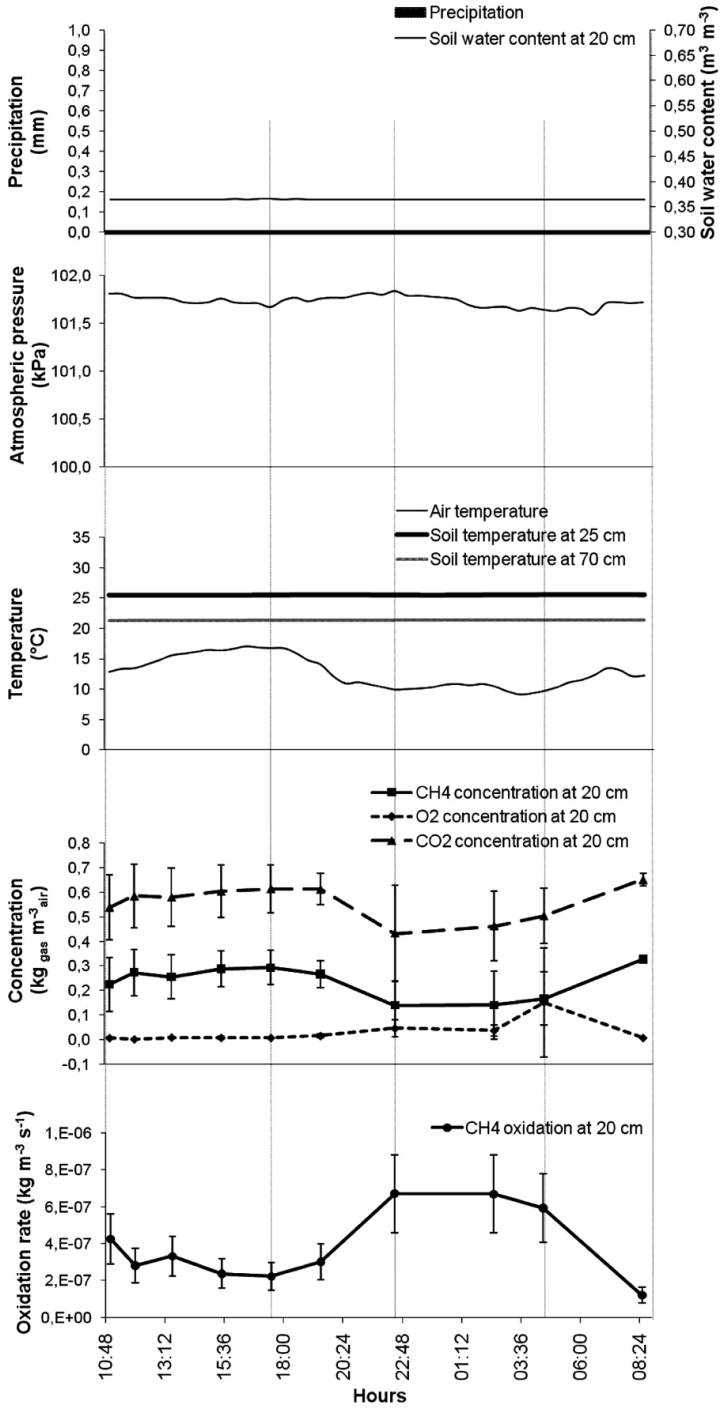
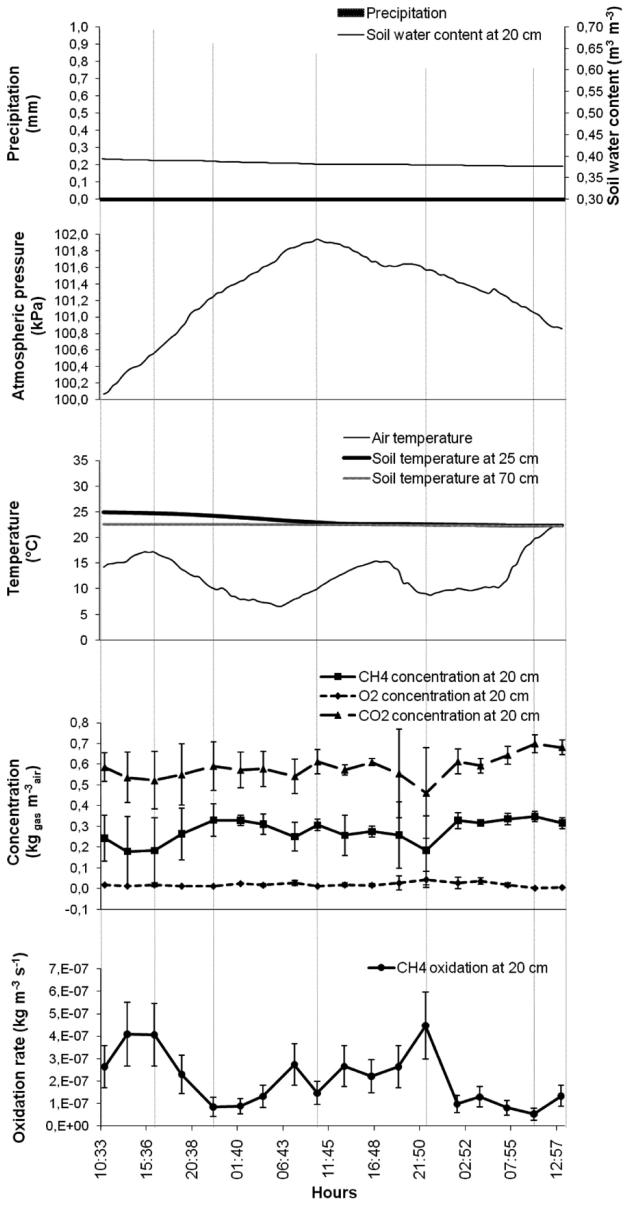


Figure 5 CH_4 oxidation rates at 0.2-m depth in the biocover and related atmospheric and soil parameters during 52 h on 12–14 September 2007 (error bars are incertitude associated to measurement precision; precipitations = 0)



3.2 Correlations and regressions with soil physical parameters

Whatever the time interval considered (months or hours), R_g was inversely correlated to CO_2 and positively to O_2 soil concentrations (Table 2, Figures 2–5). Instinctively, one may expect to obtain the opposite relationship since oxidation consumes O_2 and releases CO_2. However, the observed relationship only indicates that O_2 is a limiting

factor for methanotrophic oxidation. If the expected relationship was the only one occurring at all time, a time lag should occur, which was not the case. Also, an inverse relation between CO_2 and CH_4 concentrations eventually occurs due to biological oxidation reaction that produces CO_2 in a 1 : 1 ratio (Kjeldsen, 1996). Weaker relationships in 2006 may be due to fewer data available for regression analysis (Table 2) and to much lower variations in R_g (Figure 2 vs. Figure 3).

Optimal water content (% of dry matter) for R_g in landfill soil covers seems to be around 10–20% (Boeckx and Van Cleemput, 1996; Czepiel et al., 1996; Whalen et al., 1990), but higher thresholds up to 45% were observed for different soil types such as compost (Hilger and Humer, 2003; Humer and Lechner, 1999). The average soil water content in 2006 was much higher than this 20% threshold (Table 1). This higher soil humidity in 2006 did not favour oxidation during most of the studied period, resulting in no significant relationship between R_g and $\theta_{v0.2}$ (Table 2, Figure 2). However, if water content is reduced when soil temperature in temperate climate rise above 5°C, R_g may significantly increase (Reay et al., 2001). This was the case for the warmer period of 2007 (Figure 3), when $\theta_{v0.2}$ was about one-third lower than that of 2006 (Table 1); a strong inverse correlation is noted between R_g and $\theta_{v0.2}$ (Table 2).

Table 2 Stepwise regression coefficients of the soil parameters in relation to the oxidation rate (R_g, kg m^{-3} s^{-1}) in 2006 and 2007 and for both sequences performed in September 2007

Time	*n*	*Intercept* (kg m^{-3} s^{-1} × 10^{-6})	CO_2 (kg m^{-3} × 10^{-6})		O_2 (kg m^{-3} × 10^{-6})		$T_{0.25}$ (°C × 10^{-8})		$\theta_{v0.2}$ (m^3 m^{-3} × 10^{-6})		*P* (kPa × 10^{-8})		*Total* R^2
			A	R^2	*b*	R^2	*c*	R^2	*d*	R^2	*e*	R^2	
Year													
2006	26	–4.49	ns		0.882**	0.05	1.74**	0.09	ns		4.14*	0.04	0.82**
2007	48	2.25	–2.38***	0.89	ns		ns		–1.57**	0.01	ns		0.90**
Sequence													
24-h	19	2.89	–2.36***	0.88	ns		ns		–3.30**	0.05	ns		0.93**
52-h	35	15.9	–3.35***	0.68	–6.46**	0.04	–6.30**	0.03	–4.36**	0.07	–10.3**	0.05	0.87**

Model: R_g = Intercept + a (CO_2) + b (O_2) + c ($T_{0.25}$) + d ($WC_{0.2}$) + e (P).

R^2 associated to each parameter are partial R^2.

Parameters followed by *, **, ***, and ns are significant at $Pr > F$ of 0.1, 0.05, 0.001 and non-significant.

CH_4 oxidation occurred mainly when O_2 concentrations were between 0.05 and 0.17 kg m^{-3} (Figures 2 and 3). As a consequence of high water content in 2006, O_2 diffusion from soil surface to 0.20-m depth was compromised because of low air-filled porosity, as mentioned by De Visscher and Van Cleemput (2003), thereby reducing microbial activity and thus the value of R_g. Similarly, CH_4 diffusion from waste decomposition through the biocover is also reduced if the porosity is filled with water rather than with gas. CH_4 has then to diffuse upward through the aqueous phase of the soil, which is 10,000 times slower than in air (Hilger and Humer, 2003; Whalen et al., 1990). As a result, O_2 concentration was probably a limiting factor in 2006 and during the

52-h sequence while it was not during mid-July–mid-August 2007 and the 24-h sequence (Table 2, Figures 2–5).

CH_4 oxidation seems optimal under temperature ranging from 20°C to 25°C, in part because bacteria prefer warmer conditions (Czepiel et al., 1996; Reay et al., 2001). As air temperatures were slightly lower in 2006 than in 2007 (Table 1), the soil temperature fell well below 20°C during most of the measurement period of 2006 (Table 2, Figure 2). Comparatively, soil temperature did not seem to be a limiting factor in 2007 (Table 2) because the soil was warmer (Table 1, Figure 3). The soil temperature was also influenced by its moisture since higher water content increases heat capacity, buffering soil temperature. Wet soils are thus usually cooler, indirectly affecting R_g. In 2007, the substrate temperature was not a limiting factor since the soil had higher air-filled porosity (average 30%), but it becomes important in wet conditions (Table 2) when soil moisture is really high such as found in 2006 (Table 1, Figure 2).

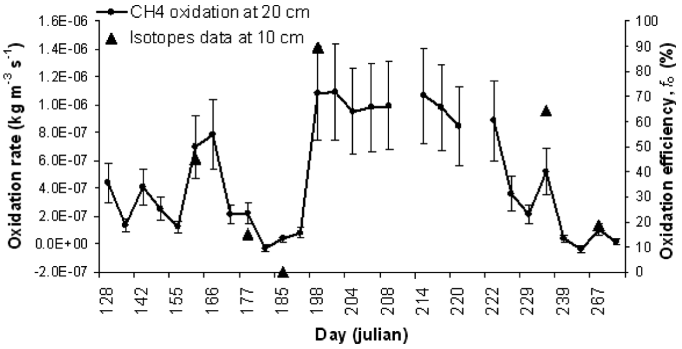
Temperature has not only a direct impact on microbial activity but also an indirect one: it influences gas movement and gas concentration, in the gas and in the liquid phases. An increase in temperature enhances gas movement, thus CH_4 upward migration, and therefore an increase in its concentration in the pores of the substrate. The results obtained are in agreement with this statement since CH_4 concentration at 0.20-m depth was positively correlated to air temperature within a day (Figures 4 and 5). Such variation in air temperature, faster than soil temperature, can create gas fluxes by a thermal gradient. This phenomenon was not accounted for in the proposed approach. Temperature gradient between waste and soil surface was not considered either. However, in this latter case, the thick GDL (Figure 1(a)) may limit the effect of waste temperature on gas movement through the biocover.

Changes in atmospheric pressure create pressure gradient and advective fluxes. CH_4 moving upward from the wastes reaches methanotrophic communities more quickly when atmospheric pressure is low, with an important effect in wet soil because gas movement is more limited than in a drier soil. Under the same conditions, oxygen movement from the atmosphere to microbial population is delayed unless strong wind pushes it into the soil, reducing the impact of pressure gradient on R_g created by change in atmospheric pressure. As a result, atmospheric pressure (P) affected CH_4 oxidation, but to a much lower extent than the above-discussed parameters during wet soil conditions (Table 2). These results support the hypothesis that changes in atmospheric pressure were limited and not accounted for in the present approach.

3.3 Validation of the proposed approach

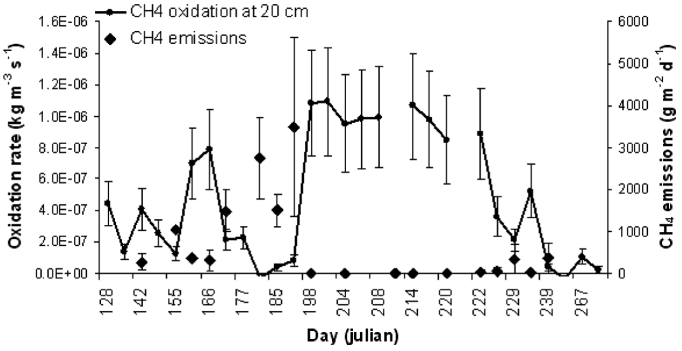
The R_g estimated with the proposed approach (and equivalent in terms of oxidation efficiencies) were compared with oxidation efficiency (f_o) obtained from stable isotope analyses performed by Cabral et al. (2010) using data from 2007 for the same site (no data available for 2006). Results from only six sampling dates were available for comparison with R_g. As shown in Figure 6, there is a strong positive correlation (Pearson $r = 0.94$, $p < 0.01$) between f_o measured at 0.1 m depth and R_g calculated at 0.2 m depth. Maximal R_g (equivalent to a calculated 98.9% oxidation efficiency) corresponds to maximal f_o value (about 90%). Differences between both approaches could be due to errors associated to the simple proposed approach, to difference in the measured depth and to high local variability.

Figure 6 CH_4 oxidation rates at 0.2-m depth in the biocover compared with stable carbon isotopes data obtained for the same site at 0.1-m depth in 2007 (error bars are incertitude associated to measurement precision)



R_g values were also compared with CH_4 surface emissions measured 17 times on the same PMOB in 2007 (Figure 7). As expected, a negative correlation was found between R_g and CH_4 surface emissions (Pearson $r = -0.51$, $p < 0.05$). Highest emissions (around 3500 g m^2 d^{-1}) were found around DOY 190 when very slight oxidation rate was estimated. In addition, maximal R_g (almost 100%, see above) corresponded to zero emission events (Figure 7). Most importantly, trends in time of R_g estimated with the proposed approach, of f_o values from the stable isotope approach (Figure 6) and of CH_4 surface emissions (Figure 7) follow the same pattern.

Figure 7 CH_4 oxidation rates at 0.2-m depth in the biocover compared with CH_4 surface emissions data obtained for the same site in 2007 (error bars for oxidation rate are incertitude associated to measurement precision and for emissions are standard deviation)



4 Conclusions

CH_4 oxidation rates, R_g, were calculated according to the proposed approach for PMOB-1, an experimental biocover installed at the St-Nicéphore landfill, Quebec, Canada. R_g ranged from 0 to 1.1×0^{-6} kg m^{-3} s^{-1}, with wide variations throughout both seasons and during the two sequences of intensive sampling. The maximal oxidation efficiency (equivalent to the maximal R_g value) obtained by the proposed approach was of comparable magnitude with the maximal CH_4 oxidation efficiency calculated by

Cabral et al. (2010) who performed a series of analyses on the same PMOB-1 following the stable isotopes approach. 100% oxidation efficiency for this PMOB-1 was also confirmed by CH_4 surface emissions.

No specific temporal trends in R_g were observed during the two short-term sequences. Comparatively on a season basis, the highest oxidation rates were observed during July and August, while nearly no oxidation occurred during the fall seasons when temperature cooled down (October and November). The majority of CH_4 oxidation occurred during a limited period when the O_2 concentration lied between 0.05 and 0.17 $kg_{\text{ of gas}}\ m^{-3}_{\text{air}}$ and the soil was warm (temperatures roughly higher than 20°C) and relatively dry, with water contents around 37% ($m^3_{\text{water}}\ m^{-3}_{\text{dry matter}}$). The results reaffirm the importance of O_2, water content and temperature for estimating CH_4 oxidation in landfill biocovers.

Additional information about temporal variability of CO_2 soil respiration, other than associated to CH_4 oxidation, would have been useful to better estimate and understand oxidation rates. Time series analyses could indicate time lags between oxidation rate and soil or atmospheric parameters, but more data are required. A more thorough validation of the proposed approach for estimating R_g, particularly using well-accepted methods, such as stable isotopes, is also needed. Further testing to validate the proposed approach should include gas concentration and water content data at every 0.05 m within the first 0.3 m of the biocover profile. This would allow better insight on the effect of dilution by atmospheric air in the upper layers of the biocover. The simple indicator approach proposed in this study for evaluating CH_4 oxidation rates may be useful to improve GHG budget with data that can easily be automated and measured at affordable cost.

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